Study on Calculation of PVT Properties of CO_2 in Supercritical States

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Keywords: equation of state, carbon dioxide, supercritical state, thermodynamic properties, calculation.

Abstract. In this paper, two equations of state, Exp-RK and 81-type Martin-Hou, were chosen and adopted to calculate P-V-T properties of CO_2 in supercritical conditions, and the deviations of calculated pressure values from reference values are presented. The mean deviations of Exp-RK equation and 81-type Martin-Hou equation are 2.16% and 2.11% respectively, and the maximum deviations are 12.4% and -3.39% respectively. Study shows that the two equations are both applicable to the calculation of P-V-T properties of carbon dioxide in supercritical states. 81-type Martin-Hou has higher accuracy for the calculation of P-V-T properties in whole region and Exp-RK equation, a cubic equation of state, is simpler and more convenient for calculation of supercritical CO_2 for engineering purposes.

Introduction

Thermodynamic properties of CO_2 in supercritical conditions are needed in engineering fields. For example, both supercritical thermodynamic properties and saturated thermodynamic properties of CO_2 are involved in the analysis of transcritical cycle of CO_2 heat pump[1,2]. In petroleum industry, CO_2 is transported through pipeline in supercritical condition for large-scale delivery[3,4]. And supercritical carbon dioxide is often used as a solvent. Thus the calculation of thermodynamic properties of CO_2 in supercritical condition is necessary.

For the purpose of calculation of thermodynamic properties of a fluid, an equation of state describing P-V-T relationship is first needed. BWR equation was chosen for determining thermodynamic properties of CO_2 in supercritical conditions and the equation constants for CO_2 were given in literature [5]. In this paper, Exp-RK equation[6] and 81-type Martin-Hou[7] are chosen for the same calculation. The former is a modified RK equation, which was intended to improve the calculating accuracy of RK equation in supercritical region so as to expand the cubic equation of state to supercritical region. 81-type Martin-Hou equation of state is one that is applicable to both saturated liquid phase and saturated vapor phase of a fluid. These two equations of state are chosen in this paper to research their accuracy of calculation for the properties of supercritical CO_2.

Choice of Equations of State

Exp-RK Equation of State. Exp-RK equation of state is a cubic equation of state and the constants of equation can be determined only with critical parameters of a fluid and therefore is convenient to use. Exq-RK equation is as follows.

$$P = \frac{RT}{V-b} - \frac{aa}{V(V+mb)} \quad . \tag{1}$$

$$m = 15.55 - 50Z_C \quad . \tag{2}$$

$$a = \Omega_a (RT)^2 / p_C \quad . \tag{3}$$

$$b = \Omega_b (RT) / p_C \quad . \tag{4}$$

$$a = \left[1 + k\left(1 - \sqrt{T / T_C}\right)\right]^2 \quad . \tag{5}$$

$$(\mathrm{m}b_C + 1) = (\mathrm{m} + 1)^{1/3} \quad . \tag{6}$$

$$z_C = 1/[3 + (\mathrm{m} - 1) b_C] \quad . \tag{7}$$

$$\Omega_a = z_C^{\,2} / b_C \; , \; \Omega_b = z_C b_C \quad . \tag{8}$$

Where P - pressure (kPa), T - temperature (K), V - molar volume (m^3 / kmol), R - gas constant (8.31451 kJ/kmol•K), P_C - critical pressure (kPa), T_C - critical temperature (K), Z_C - critical compressibility factor. For CO_2, T_C=304.2K, P_C=7376kPa, Z_C=0.274[8]

81-type Martin–Hou Equation of State. Original Martin-Hou equation was improved to extend to liquid phase in 1981, and is known as 81-type Martin–Hou equation of state in literature(abbr. *81 M-H equation* in this paper).*81 M-H equation* has high accuracy of calculation for both saturated liquid and saturated vapor. Since it was published, *81 M-H equation* has been widely applied [8, 9]. Literature [6] provided the constants of *81 M-H equation* for saturated liquid and saturated vapor of CO_2. This paper chooses *81 M-H equation* and these constants of CO_2 in literature [6] to research the applicability and accuracy of *81 M-H equation* and these constants for the calculation of supercritical CO_2. *81 M-H equation* is as follows

$$p = \frac{RT}{V-b} + \frac{A_2 + B_2 T + C_2 e^{-kT/T_e}}{(\mathrm{V-b})^2} + \frac{A_3 + B_3 T + C_3 e^{-kT/T_C}}{(V-b)^3} + \frac{A_4 + B_4 T}{(V-b)^4} + \frac{B_5 T}{(V-b)^5} \quad . \tag{9}$$

Where k = 5.475, p - pressure (atm), T - temperature (K), V - mole volume (cm^3 / gmol), R- gas constant(82.055 atm•cm^3/K•gmol). For CO_2, the constants of the Eq.(9) are shown in Table 1.

Table 1 Cconstants of 81 M-H equation for CO_2

A_2	B_2	C_2	A_3	B_3	C_3
-4519295.4	4676.0096	-79266871	327671590	-380994.25	5855596400
A_4	B_4	B_5	b	T_C[K]	
-12896697200	15508608	374367850	20.188074	304.2	

Results and Discussion

The temperature range and pressure range of calculation are from 310 K to 600 K and from 7.5 MPa to 10 MPa respectively. The results and deviations of pressure calculation of Exp-RK equation and 81 M-H equation are shown in Table 2 and Table 3. Values in the columns T, V, and p are taken from literature [5, 10].

Deviation of calculation is determined according to

$$d_i = (P_i - P_{cal,i}) / P_i \times 100\% \quad . \tag{10}$$

Where $p_{cal,i}$ is the pressure value calculated with Eq.9 or Eq.10, and p_i is the reference value of pressure.

Mean deviation of calculation is determined according to

$$d_{mean} = \sum_{1}^{N} |d_i| / N \ . \tag{11}$$

Where N is the number of calculation points.

Table 1 Calculation results of Exp-RK equation

T [K]	V [cm^3/gmol]	P [bar]	P_{cal} [bar]	δ_i [%]	T [K]	V [cm^3/gmol]	P [bar]	P_{cal} [bar[	δ_i [%]
310	173.01	75	73.812	1.58	400	382.38	75	73.767	1.64
310	133.0	80	79.123	1.10	400	354.74	80	78.708	1.62
310	71.494	90	97.565	-8.41	400	308.76	90	88.616	1.54
310	64.102	100	112.488	-12.49	400	272.1	100	98.571	1.43
320	216.62	75	73.421	2.11	500	526.6	75	74.132	1.16
320	189.6	80	78.455	1.93	500	492.16	80	79.098	1.13
320	140.08	90	88.899	1.22	500	434.87	90	89.041	1.07
320	97.919	100	101.088	-1.09	500	389.14	100	99.005	0.99
350	292.83	75	73.429	2.09	600	654.73	75	74.265	0.98
350	267.84	80	78.353	2.06	600	613.33	80	79.238	0.95
350	225.95	90	88.274	1.92	600	544.4	90	89.192	0.90
350	192.26	100	98.328	1.67	600	489.34	100	99.157	0.84
δ_{mean} (%)		2.16							
δ_{max} (%)		-12.49							

As can be seen from Table 2, the deviations of calculation values of pressure from reference values are, on the whole, small, the average deviation being only 2.16%. That shows that Exp-RK equation has a reasonable accuracy of calculation in supercritical region of CO_2 , though the equation has a simple form.

Table 3 Calculation results of 81 M-H equation

T [K]	V [cm^3/gmol]	P [bar]	P_{cal} [bar]	δ_i [%]	T [K]	V [cm^3/gmol	P [ba]r	P_{cal} [bar]	δ_i [%]
310	173.01	75	73.668	1.78	400	382.38	75	73.393	2.14
310	133	80	78.533	1.83	400	354.74	80	78.211	2.24
310	71.494	90	90.364	-0.40	400	308.76	90	87.804	2.44
310	64.102	100	103.391	-3.39	400	272.1	100	97.340	2.66
320	216.62	75	73.514	1.98	500	526.6	75	73.462	2.05
320	189.6	80	78.296	2.13	500	492.16	80	78.308	2.12
320	140.08	90	87.858	2.38	500	434.87	90	87.971	2.25
320	97.919	100	98.411	1.59	500	389.14	100	97.600	2.40
350	292.83	75	73.452	2.06	600	654.73	75	73.696	1.74
350	267.84	80	78.247	2.19	600	613.33	80	78.578	1.78
350	225.95	90	87.777	2.47	600	544.4	90	88.323	1.86
350	192.26	100	97.226	2.77	600	489.34	100	98.044	1.96
δ_{mean} (%)		2.11							
δ_{max} (%)		-3.39							

As can be seen from Table 3, the deviations of the calculation values of pressure from reference values are quite small in all states. The average deviation is only 2.11% and the maximum deviation -3.39%. *81 M-H equation* remains satisfactory accuracy of calculation in supercritical region of CO_2.

Conclusion

In this paper, Exp-RK equation of state and 81-type Martin-Hou equation of state are chosen for the calculation of PVT properties of CO_2 in supercritical states. The deviations of both equations for pressure calculation are small. 81-type Martin-Hou equation remains good accuracy of calculation in supercritical region of CO_2, and can be used to calculate CO_2 properties in both supercritical region and saturation region. Exp-RK equation of state is simple in form and convenient in use, and has reasonable accuracy in supercritical region of CO_2, and therefore it is a proper choice for the calculation of properties of supercritical CO_2 for engineering purposes.

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